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FATIGUE EFFECTS IN THE LUMINESCENT YIELD OF SODIUM SALICYLATE*

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INTRODUCTION

Sodium salicylate sensitized photomultipliers have been used for many years as photon detectors in the near and vacuum ultraviolet spectral region. This is due to the fact, reported by several authors[1,2,3], that the phosphor possesses the desirable property of having a luminescent efficiency which is essentially independent of the wavelength of the incident radiation. While using sodium salicylate in our laboratory, in the course of measurements in the vacuum ultraviolet, it was noticed that there was an apparent decrease in the intensity of the radiation emerging from the exit slit of the monochromator with time, particularly at shorter wavelengths, as measured with the phosphor-photomultiplier combination. This decrease was at first attributed to a decline in grating efficiency or a change in source characteristics, or both, but measurements with a calibrated radiation thermocouple showed that this was not the case. A return to the initial spectral distribution upon application of a fresh phosphor coating showed that the sodium salicylate itself had declined in sensitivity. More detailed experiments showed that the decline in the response of the phosphor was due to a combination of two effects, a preferential decrease at shorter wavelengths due to prolonged exposure to the atmosphere of the monochromator and a general decline at all wavelengths due to exposure to a large number of energetic, $h\nu \geqslant 7.7$eV, photons.

EXPERIMENTAL

The monochromator used in this work was a 40cm normal incidence instrument designed by Dr. K. J. Teegarden of this laboratory. Detailed descriptions are found elsewhere[4,5]. The radiation source was a quartz discharge lamp, operated on hydrogen, which was open at one end. The radiation from the lamp passes through a variable entrance slit, is dispersed by the grating and then passes through a variable exit slit into the sample chamber, a "reflectometer", designed by one of us (AMS)[6]. Figure 1 shows a schematic diagram of this device. The radiation thermocouple used in our work was fabricated by Charles M. Reeder and Company and was mounted in a special holder for insertion in the rear accessory port of the reflectometer.

For measurements in which the effect on the response of the phosphor of prolonged exposure to the environment of the monochromator (environmental fatigue in the following) was determined, the entire face of the probe, shown in Figure 1, was coated with sodium salicylate. By comparing the luminescent signal seen by the photomultiplier with the signal seen by the thermocouple the relative quantum yield of the phosphor layer, η_{rel}, defined as

$$\eta_{rel} = \frac{\text{photomultiplier signal}}{\lambda \times (\text{thermocouple signal})}$$

could be measured. These measurements were continued over a period of time, with the sample maintained in the interior of the monochromator so that the time dependence of this environmental fatigue could be determined.

For determinations of the effect of intense radiation on the response of the phosphor, referred to as radiation fatigue, the probe was coated in two sections separated by an uncoated strip in the center. One side was then irradiated with a known number of quanta, of energy $h\nu_0$, while the other coated section was kept out of the beam for comparison purposes. At specified intervals the response of the irradiated section was compared to that of the unirradiated section. The resultant ratio was thus a measure of the change in response brought about by irradiation.

RESULTS

Figure 2 shows the relative quantum yield of a representative sodium salicylate sample as a function of time in the environment of the monochromator. The total amount of radiation to which the layer had been exposed during this study was much smaller than that required to cause appreciable radiation damage (see following paragraphs). The decrease in response is obvious and is more pronounced at shorter wavelengths. If the values of the response at a given wavelength are plotted against time there is some indication of a dependence of the form

$$\eta(t) = \eta(o)e^{-\alpha(\lambda)t}$$

The step-like decrease noted in the response of a freshly prepared layer is shown in more detail in Figure 3 and will be discussed in a later section.

Figure 4 shows plots of the ratio of the signals from the irradiated and control sides of the probe vs total number of photons incident. The number labeling each curve refers to the energy of the irradiating photons. It is seen that there is a definite decrease in response and that for a given number of photons the decrease is larger for photons of greater energy. These sodium salicylate layers were prepared under essentially identical conditions so that each layer should contain approximately the same number of molecules. This number, of the order of 10^{17} mol/cm^2, was obtained by accurate weighing of identically prepared layers. For a given photon energy somewhat thinner layers show a slightly more rapid decrease in response than those above, while thicker layers are somewhat less sensitive to the radiation fatigue. Experiments in which the sample was irradiated by the zero order beam from the monochromator filtered to remove all wavelengths shorter than 1600Å, have shown that there may be a photon energy threshold for the fatigue effect, for although the total amount of energy incident was comparable to or greater than that employed using higher energy photons, no decrease in response was observed.

In addition to the data shown in Figure 4 some information is available for $\lambda = 584\mathring{A}$. The measurement of photon flux is very difficult at this wavelength due to the low intensities available; however, there is indication that these photons are still more effective in producing a decrease in response than those of lower energy.

DISCUSSION

At present we are unable to explain the fact that the relative quantum yield of sodium salicylate, as measured with our apparatus, is not by any means flat. We have attempted to find some systematic error which would cause the observed behavior, but to date have been unable to do so and must therefore leave the disagreement with earlier data as an unresolved question. In this paper we are concerned only with changes in the yield and so, although somewhat disconcerting, the initial shape of the yield curve does not effect our measurements.

Hamann[3] has stated that the response of sodium salicylate samples maintained in air for periods of a year or more shows no appreciable decline, so that the decrease found here is definitely a result of exposure to the atmosphere of the monochromator. This decline in yield may be connected with (1) the formation of an absorbing layer on the phosphor (this suggestion seems to be supported somewhat by the fact that the decrease is more pronounced at shorter wavelengths); (2) possible chemical reaction with some constituent of the monochromator atmosphere or; (3) evaporation of portions of the coating. Lacking more detailed information about the mechanism of the luminescence and the chemical properties of sodium salicylate however, such suggestions must remain speculation.

The fact that the radiation-induced damage appears to possess an energy threshold and that the number of quanta required to cause appreciable damage is of the same order of magnitude as the number of molecules in the phosphor coating seems to indicate that some sort of photochemical reaction is occuring. This may be an actual decomposition of the phosphor, or as suggested before, a reaction with substances in the monochromator environment. An observation pertinent to this discussion is the fact that we have noticed a rather strong luminescence, under 2537Å excitation, from those parts, and only those parts, of the light baffles which intercept portions of the beam, particularly the 0-order, inside the monochromator.

CONCLUSION

The principal goal of this work was not to present detailed explanations of the observed effects but merely to point out that these effects do exist and that because of them certain precautions should be observed in the use of sodium salicylate. The essential precaution, on the basis of the reported data, is that the coatings should be renewed at rather short intervals and that the atmosphere of the monochromator be kept as clean as possible.

ACKNOWLEDGEMENT

We wish to thank Professor D. B. Dutton for his continued interest and encouragement during the course of this work.

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6. A. Smith, J. Opt. Soc. Am. 50, 862 (1960)

LIST OF FIGURES

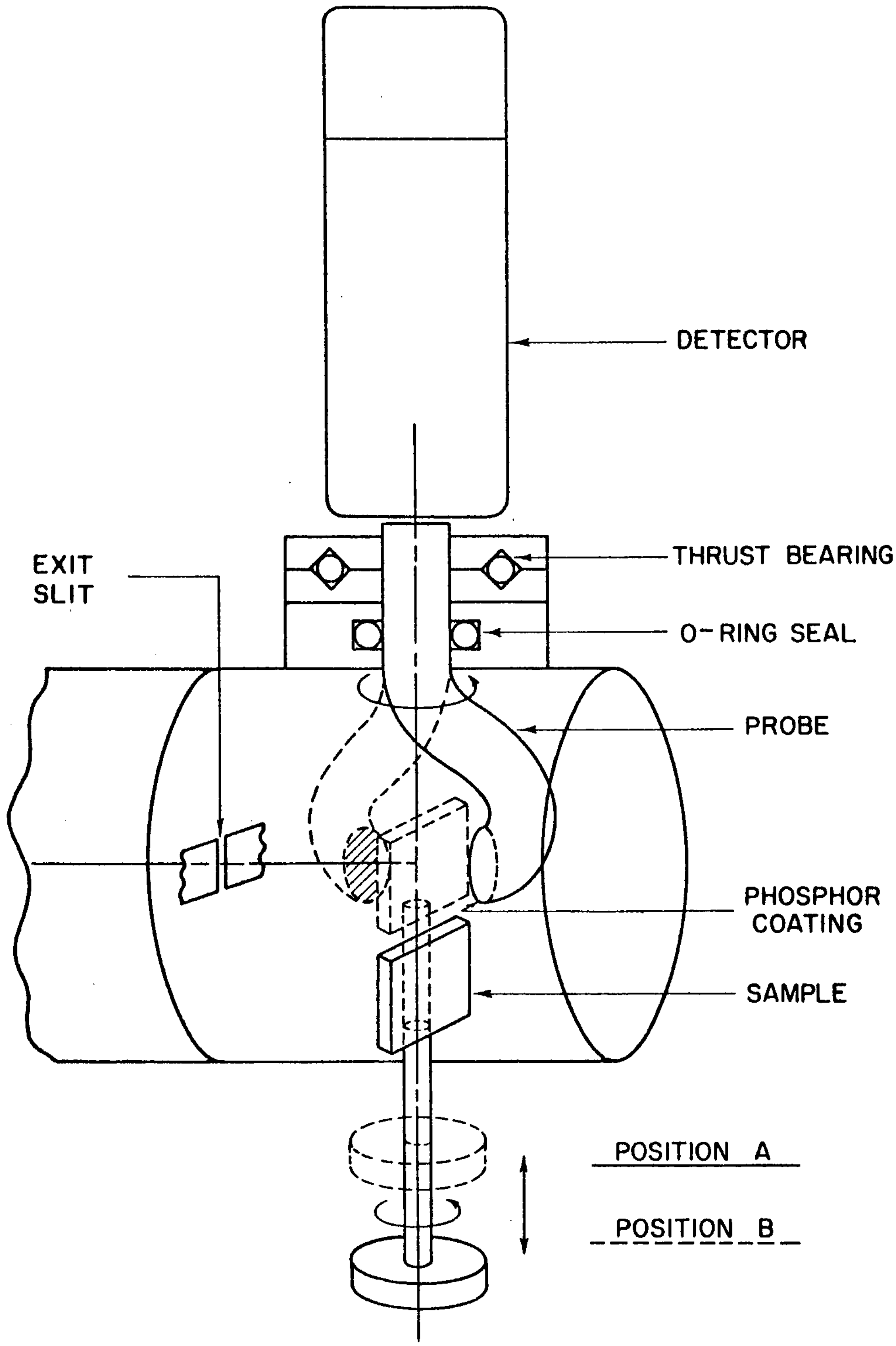

Figure 1 Schematic arrangement of the "reflectometer" used in this work.

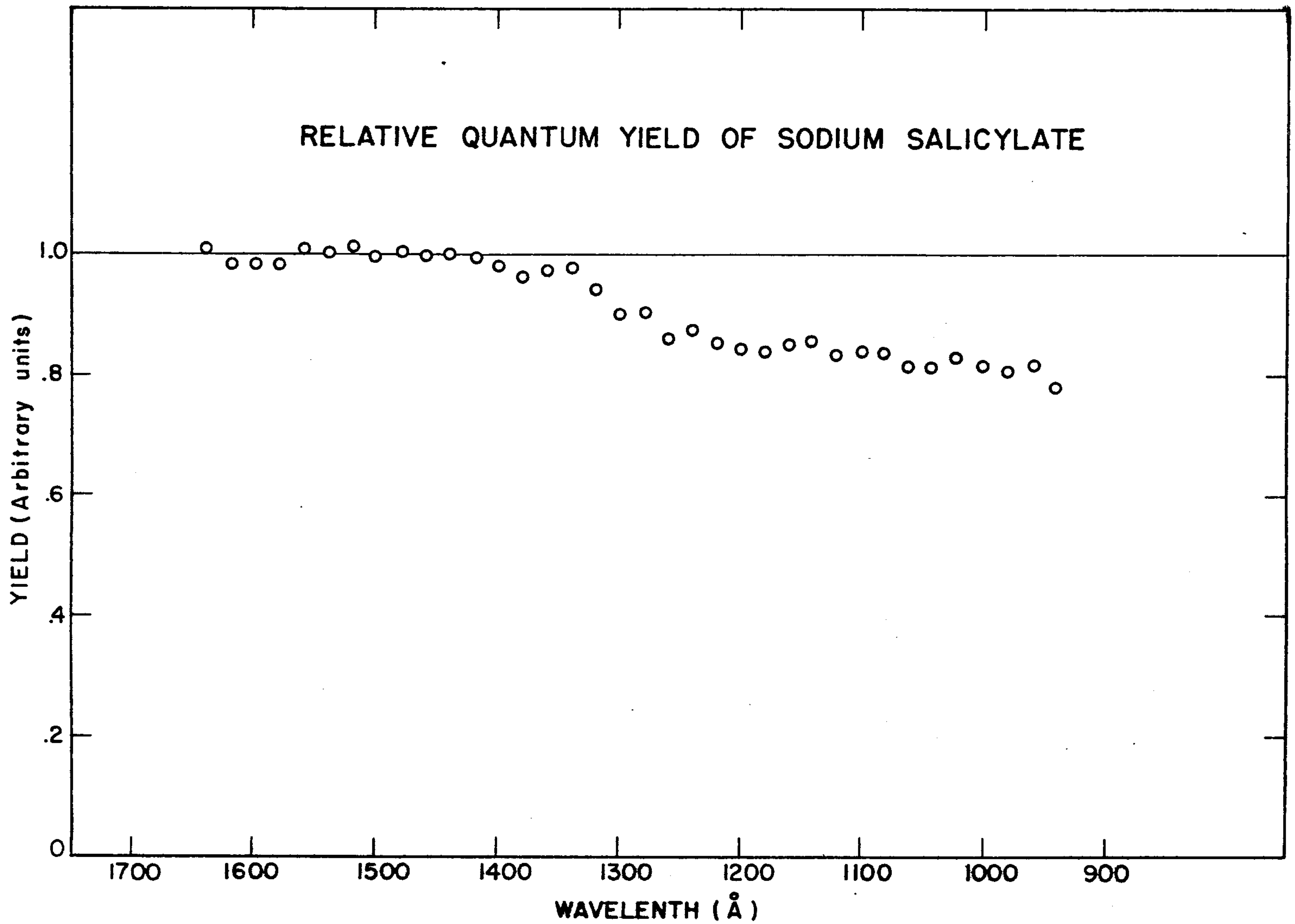

Figure 2 Relative quantum yield of a sodium salicylate sample as a function of time in the atmosphere of the monochromator.

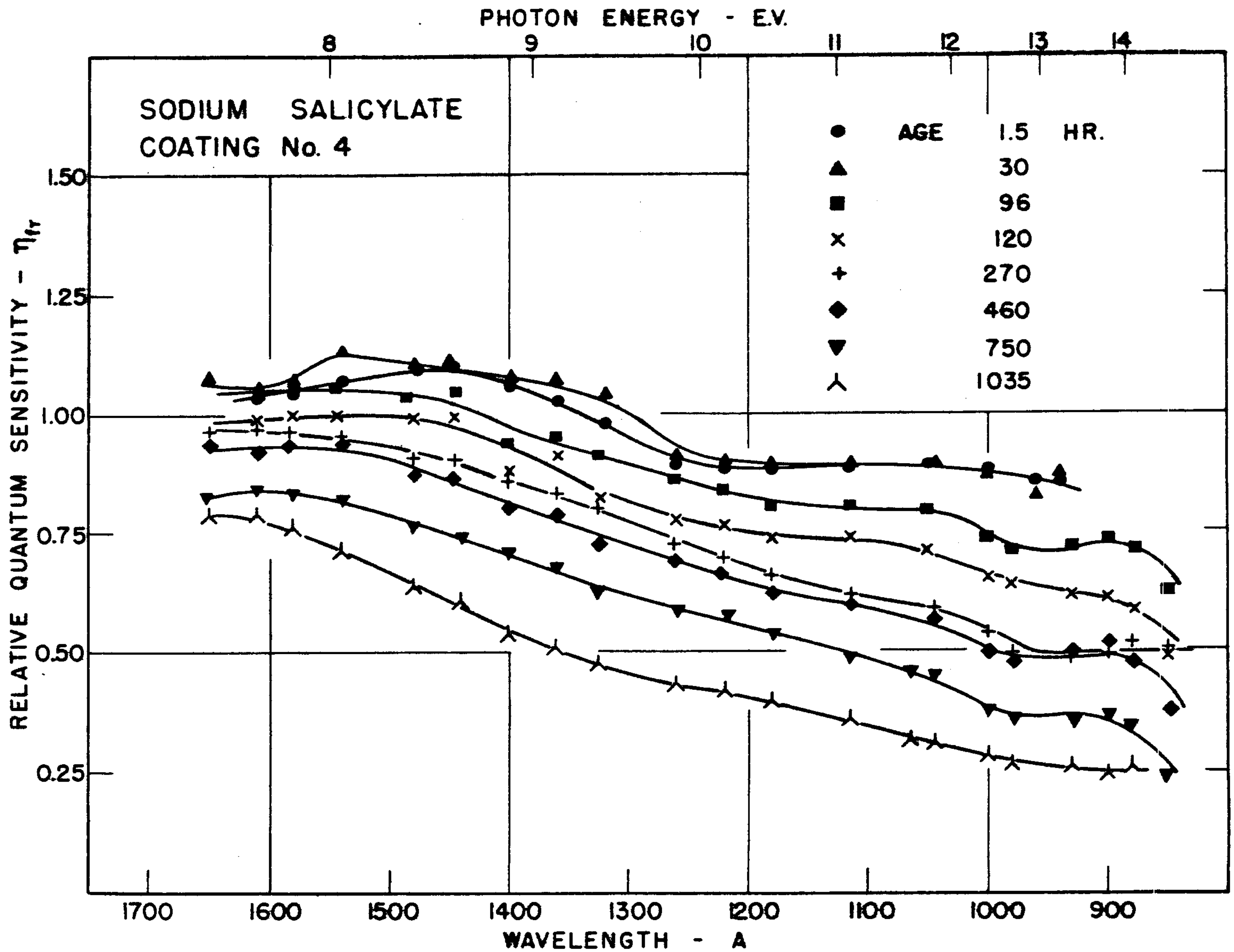

Figure 3 Relative quantum yield of a freshly prepared sodium salicylate sample.

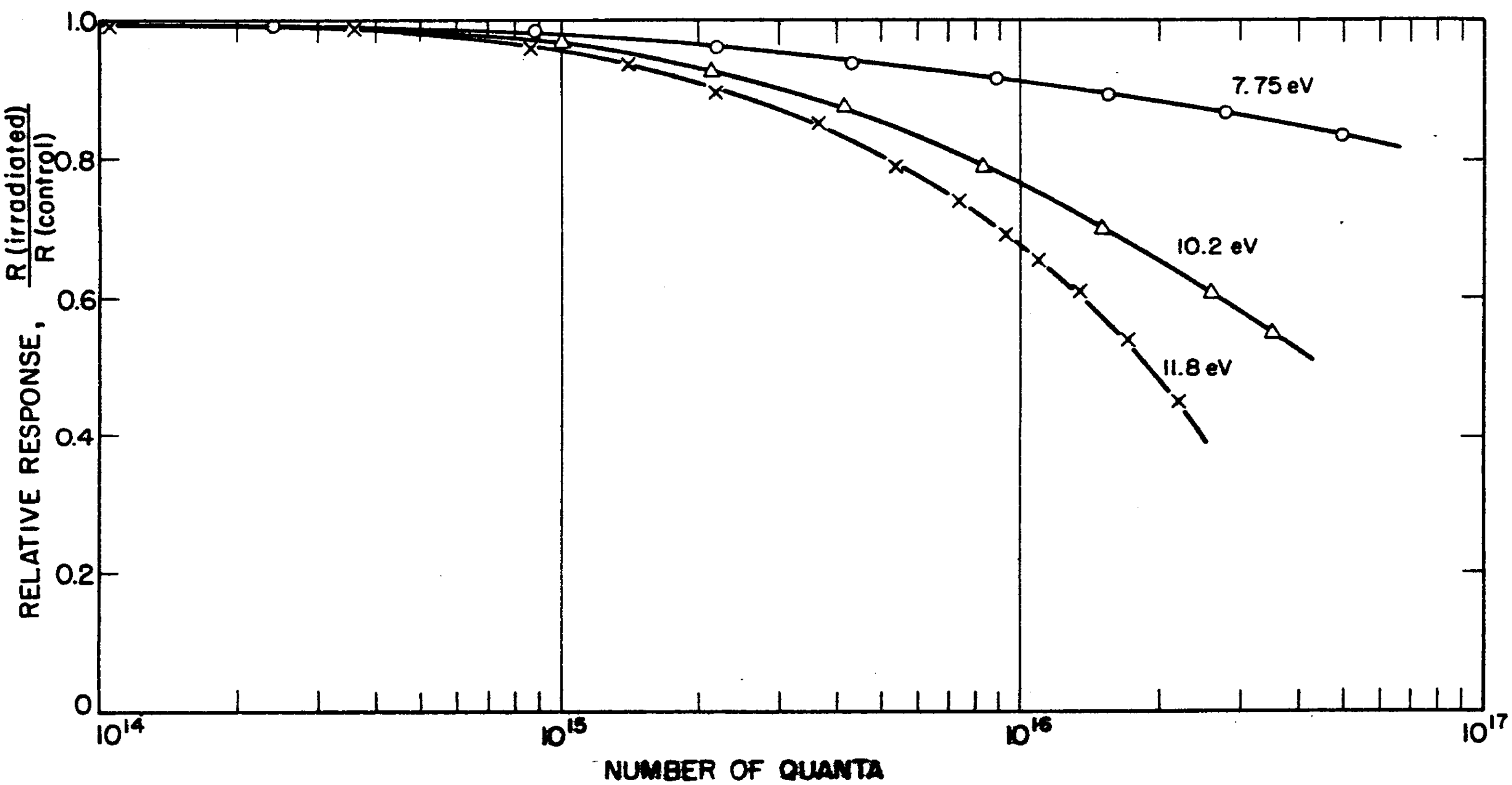

Figure 4 Irradiation fatigue study of sodium salicylate films. Numbers labeling each curve refer to the energy of the photons used to produce the decline in response.